FREE AND BOUND EXCITON LUMINESCENCE OF ZnP_2 –D_4^8

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Abstract

Thin structure of polarized absorption spectra of indirect transitions with phonon emission in the ZnP_2 crystals is investigated. In the luminescence spectra, radiation of phonons at annihilation of free excitons simultaneously with radiation of excitons bound on axial centre is found. A model of optic recombination transitions of the axial centre is proposed.

Introduction

Development of element base for polarization optoelectronics (design of devices for polarization optoelectronics) requires research and information on optic and electron properties of strongly anisotropic materials allowing us to invert conductivity type. Anisotropy of optic, electric and other properties of semiconductors calls forth many potential possibilities to design devices with specific characteristics [1, 2]. Most urgent is investigation of properties of the anisotropic materials whereof active elements, p-n transitions, surface-barrier diodes and other optoelectronic devices are obtained. Compound ZnP_2 belongs to these materials [2-7].

In the present work new information on thin structure of spectra of absorption and luminescence in doped and nondoped crystals of zinc diphosphide of tetragonal modification at 9 K is obtained. Superposition of vibron luminescence of free excitons and luminescence of excitons bound on axial centre is found.

Experiment methods

Single crystals ZnP_2 are obtained from the gaseous phase in the form of ingots having the sizes 1x1x2 cm, their long side being as a rule parallel to the crystal axis. Optic spectra of absorption and luminescence are measured in cryostat LTS-32C330 Workhorse-typ Optical with the help of double Raman spectrometer with the light force 1:5 and dispersion of 5 A/mm. Absorption spectra at 2 K and 4.2 K are measured in a glass cryostat in liquid He.

Results and discussion

Optic properties of tetragonal zinc diphosphide were studied in many works, where an indirect character of minimal energy gap is found and values of E_g and of energies participating in the phonon transition are determined [5-9].

Edge absorption a-ZnP_2 measured at the temperatures 2, 77 and 300 K for two polarizations of incident light contains a number of peculiarities. Absorption curves at room temperature do not contain visible peculiarities. At 77 K absorption increase is flat in the longwave region and it is sharper at high values of the absorption coefficient. The curves taken in the polarized light cross in the points P_1 (2.195 eV) and P_2 (2.340 eV).

At the temperature 2 K the absorption curve has three sections with different inclinations. One can obviously see the absorption increase in the longwave region, then flatter section in the energy range 2.30-2.38 eV and sharper increase of absorption in the region of 2.40 eV, where the absorption coefficient achieves the values 10^3-10^4 cm^{-1}. Beginning of each of these sections is characterized by the energies E_{g1}=2.21, E_{g2}=2.30, E_g^{Π}=2.40 eV [5, 6].

In the region of small absorption coefficients (E_{g1}) one can see strongly pronounced step-like structure in both polarizations. These curves are well described by the theoretical dependence K(hυ) for allowed indirect transitions, E_{g1} being the threshold value of phononless indirect transition in the excitons band, and thresholds $a_1 - a_4$ and $b_1 - b_4$ are determined by transitions with emission of phonons.

In the region E>2.25 eV in polarization E||c a second group of steps C1-C4 is observed, it is interpreted by indirect transitions with phonon emission in higher energy exciton band 2.274 eV. In the region of high absorption coefficients the absorption dependence on energy of light photons is well described by the expression for direct allowed transitions [5, 6].

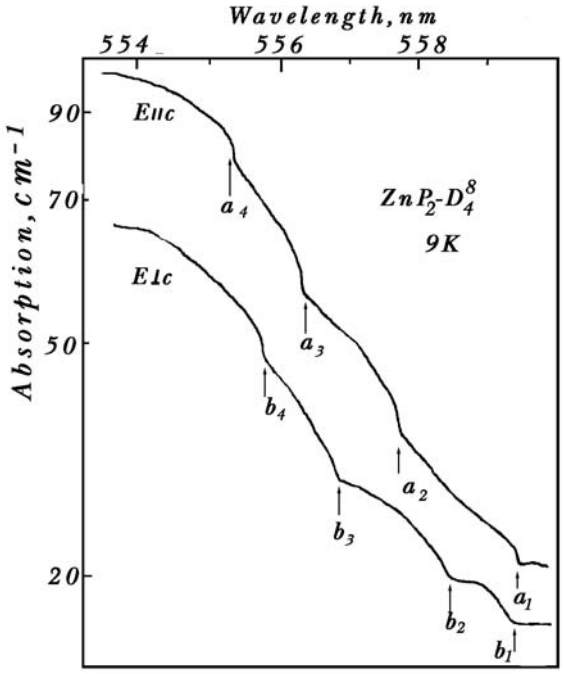

Fig. 1. Edge absorption spectra of the crystals ZnP_2 at 10 K.

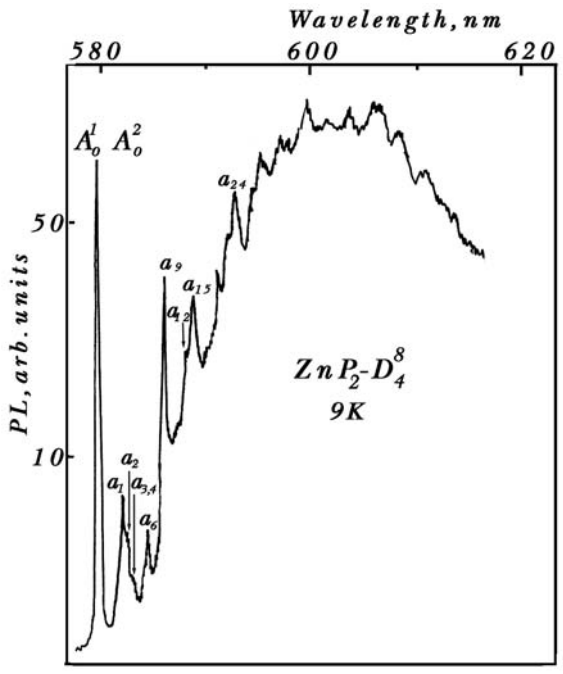

Fig. 2. Vibron spectra of the radiation of free excitons of the crystals ZnP_2 at 10 K.

Fig. 1 shows absorption spectra in the longwave region of specially nondoped crystals ZnP_2 at 10 K in polarizations E||c and E⊥c. The absorption curves are due to indirect transitions E_{g1} with phonon emission. These measurements are carried out for single crystals wherein short-wave bound excitons $A_0^1 - A_0^2$ described in detail in [5, 6] were not found. At the same time the steps determined by indirect transitions with phonon emission obtained in this work and reported in [5, 6] practically coincide (Table 1).

Fig. 2 shows photoluminescence spectra of specially nondoped crystals ZnP_2 at 10 K in the short-wave region, i.e. in the region adjoining the free exciton level. At the energy 2,2085 eV a weak peak of luminescence is found, according to the edge absorption data it

coincides with the radiation energy from the free exciton level. We explain peculiarity x_1 - x_{10} in the luminescence spectra by phonon replicas of the free exciton recombination.

The band x_i is behind the free exciton energy E_{gx}^{lib} by the value of optic phonons (Table 1) [10-13]. In the luminescence spectra various optic phonons can take part. The crystals ZnP_2 - D_4^8 have the structure described by the space group D_4^8 (D_4^4). 8 formula units, i.e. 24 atoms will go into unit cell, in the general case the number of phonon branches is equal to 72. In the centre of the Brillouin zone the lattice oscillations correspond to the following irreducible representations $9A_1 + 9B_1 + 9A_2$ $9B_2$ and 18E. Optic phonons are described by representations A_1, B_1, B_2 and E, which are active in the Raman scattering. Optic phonons of symmetry $8A_2$ and 17E are active in the infrared reflection spectra [10-13]. Availability of this quantity of oscillation modes makes it possible to observe radiation of free excitons with emission of many phonons.

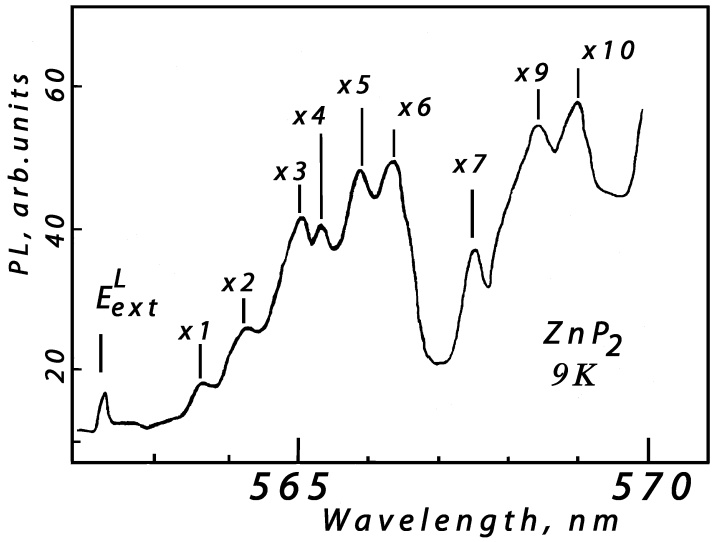

Fig. 3. Vibron spectra of the radiation of bound excitons of the crystals ZnP_2 at 10 K.

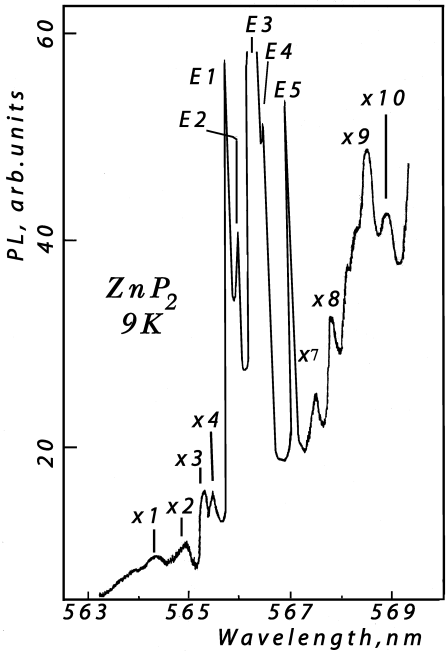

Fig. 4. Superposition of radiation spectra of the bound excitons (E_0^1 - E_0^5) and phonon replicas of free excitons (X_1-X_{10}) in the ZnP_2 at 10 K.

The survey luminescence spectrum of crystals weakly doped with uncontrollable impurity (hypothetically Mn, an increased concentration of this element was found in the initial components P) is shown in Fig. 3. In these samples narrow lines E_0^1, E_0^2 and their phonon replicas are found.

Fig. 4 shows thin structure of radiation spectra in the short-wave region. In the spectra, phonon radiation at annihilation of free exciton (x_i) simultaneously with radiation on bound excitons $\left(E_0^1 - E_0^5\right)$ is found. Phononless lines of radiation of bound exciton E_0^1(2,19515 eV), E_0^2(2,19440 eV), E_0^3(2,19287), E_0^4(2,19277) and E_0^5(2,18987) are seen as narrows lines. The bands x_i are hundreds times weaker and they have halfwidth being practically by an order larger than the lines $E_0^1 - E_0^5$. These two types of lines x_i and $E_0^1 - E_0^5$ of the radiative recombination are observed simultaneously practically in one and the same energy interval.

At the thermodynamic equilibrium and assumption of degeneration absence the radiative recombination velocity is determined by the ratio [15]:

$$R = \frac{8\pi k_B^3 T}{c^2 h^3} \int_0^\infty \frac{n^2 U^2 K du}{e^u - 1}$$

where k_B is the Boltzmann constant, c is the velocity of light, h is the Plank constant, T is the temperature, n is the charge carrier concentration, k is the absorption coefficient, $U = \frac{h\upsilon}{k_B \pi}$.

It proceeds from this expression that the same transitions, which form the absorption coefficient may participate in recombination.

The spectral distribution of absorption for indirect transitions in the exciton band with absorption and emission of phonons has the form:

$$K(\hbar\omega) = \frac{A\left(\hbar\omega - E_g + E_{p1} + G_{\text{ext1}}\right)^2}{e^{E_{p1}/kT} - 1} + \frac{A\left(\hbar\omega - E_g - E_{p1} + G_{\text{ext1}}\right)^2}{1 - e^{-E_{p1}/kT}} +$$

$$+ \frac{A'\left(\hbar\omega - E_g + E_{p2} + G_{\text{ext2}}\right)^2}{e^{E_{p2}/kT} - 1} + \frac{A'\left(\hbar\omega - E_g - E_{p2} + G_{\text{ext2}}\right)^2}{1 - e^{-E_{p2}/kT}}$$

The first two items determine indirect transitions with absorption and emission of phonon E_{p1} in the exciton band G_{ext1}, and two last items determine indirect transitions with absorption and emission of phonon E_{p2} in the exciton band G_{ext2}. Expression (1) shows that both transitions are possible simultaneously in the exciton bands G_{ext1} and G_{ext2} correspondingly, under the condition that

$$E_{p1}=G_{ext1}-G_{ext2}+E_{p2}.$$

Here the indirect transitions with absorption of phonons are determined by the following items:

$$K(\hbar\omega) = \frac{A\left(\hbar\omega - E_g + E_{p1} + G_{\text{ext1}}\right)^2}{e^{E_{p1}/kT} - 1} + \frac{A'\left(\hbar\omega - E_g + E_{p2} + G_{\text{ext2}}\right)^2}{e^{E_{p2}/kT} - 1} = K_{a1}(\hbar\omega) + K_{a2}(\hbar\omega)$$

The absorption described by both items is two independent processes taking place in the first and the second exciton band correspondingly. Absorption with emission of two and more phonons in one exciton band is described by the expression:

$$K_e(\hbar\omega) = \frac{A\left(\hbar\omega - E_{gx} + E_{p1} + G_{\text{ext1}}\right)^2}{e^{E_{p1}/kT} - 1} + \frac{A'\left(\hbar\omega - E_{gx} + E_{p2} + G_{\text{ext2}}\right)^2}{e^{E_{p2}/kT} - 1} + \ldots$$

As it is known, in the unit cell of the crystal ZnP_2 there are many atoms (N=24), this determining big quantity of oscillation modes of different symmetry [10-13] in the wide energy range.

At the temperature 10 K in the crystals ZnP_2 the energy distance between the level of free (G_{ext1}) and bound E_0^1 (G_{ext2}) excitons is equal to 13,3 meV, and optic phonons achieve the energy value of 59.5 meV. Hence, exciton levels of bound (E_0) and free exciton (E_{gx}) satisfy the condition $E_{p1}=G_{ext1}-G_{ext2}+E_{p2}$.

In ZnP_2-D_4^8 there are found 18 polar oscillation modes only of E-symmetry (Γ-phonons) being active in the Raman and IR-spectra (7.3, 10.6, 13.4, 16.4, 22.4, 22.8, 25.4, 29.0, 31.1, 34.7, 40.0, 41.9, 45.0, 53.3, 57.5, 59.5 meV) [10-13]. Besides, there are active modes of other symmetries. This set of oscillation modes may ensure conditions for transition at the same energies in the exciton band with participation of phonons being different in size,

for example, with participation of a big phonon and the one being somewhat less in energy. These two processes superimpose each other, here the total absorption and even the interfering one may be shown. Analogous dependence takes place in luminescence.

Thus, the process of recombination radiation may occur simultaneously from two centres. The radiation caused by annihilation of free excitons leads to appearance of a row of bands (x_i) in the longwave region from E_{ext}^{lib} (2,2085 eV) at the energy distance being equal to the energy of optic phonons.

The radiated energy of the phonon may coincide with the energy position of the level of forbidden states of bound exciton. At the free exciton annihilation (E_{gx}^{lib}=2,2085 eV) the phonon radiative band different from E_{gx}^{lib} at the energy distance 13,3 meV is observed. There is such a phonon of the symmetry E, it is radiated at the energy 2,1951 eV. This radiative band coincides with the energy position of the level of bound exciton E_{0x}^{1} (2,19515 eV) and is close to E_{0x}^{2} (2,19440 eV). E_{gx}^{lib} (2,2085 eV) - E_{gx} (13,3 meV) = E_i (2,1952 eV). Such a coincidence of energies of phonon radiation resulting from the free exciton annihilation with the energy levels of bound excitons may remove a ban of optic transitions from the levels of bound exciton, which is put by rules of the bound exciton selection.

In zinc diphosphide the electron transitions forbidden in the dipole approximation become allowed with the phonon participation. This regularity is realized in all semiconductor crystals.

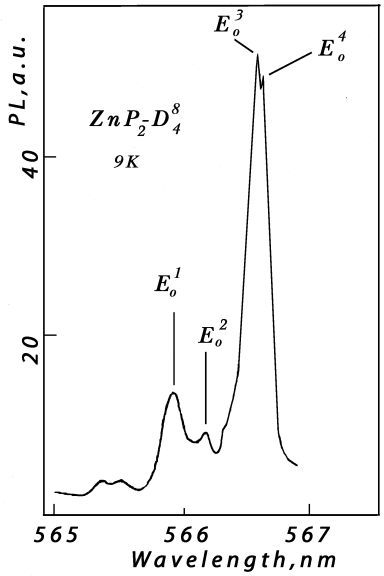

Fig. 5. Thin structure of the no-phonon lines of bound exciton in the ZnP_2 at 10 K.

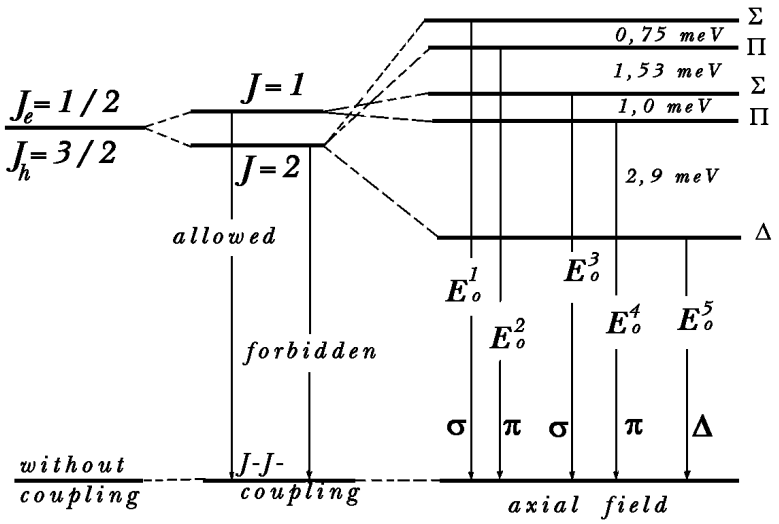

Fig. 6. Electron transitions of the exciton bound on axial centre in the ZnP_2.

In [5, 6] and in this paper we consider that narrow lines $E_0^1 - E_0^5$ are due to phononless lines of the exciton bound on axial centre. The exciton consisting of the electron with spin 1/2 and hole with spin 3/2 bound on the centre with the axial symmetry forms (from the level J=1) two levels (Σ and Π)[14]. Optic radiative transitions from the levels Σ and Π (J=1) are allowed and they determine phononless lines E_0^3 and E_0^4. These lines are the most intense and they disappear with the temperature growth (≈40 K) [5, 6]. These lines are split by small

value (~0,1 meV) (Fig. 5). The state with J=2 under the action of the axial field is split into three levels Σ, Π and Δ. Transitions from these levels are forbidden by the selection rules. The phonon energy radiated by the crystal in the result of the free exciton annihilation in the luminescence spectra corresponds to the energy of radiation of the bound exciton forbidden transition. This leads to the resonance excitation of the bound exciton forbidden states and to the removal of the ban and intensification of luminescence from the forbidden levels. Fig. 6 shows the energy diagram of levels of the exciton bound on axial centre. The radiation lines E_0^3 and E_0^4 are determined by allowed transitions from the zones of symmetry Σ and Π correspondingly. These levels are split by the crystal axial field of the centre whereon the exciton is bound. The radiation lines E_0^1 and E_0^2 are split by 0,75 meV and they are due to the levels Σ and Π of the forbidden state of the bound exciton (Fig. 6). Spin-orbit interaction also leads to the state splitting and appearance of the level Δ. The energy distance between Σ(Π)-Δ determines the value of the level splitting due to spin-orbit interaction (Δ_{SO}).

In this model the value of splitting due to the spin-orbit interaction is larger than the value of splitting due to the crystal field (Fig. 6). The energy interval between Σ-Σ levels is equal to 2,2 meV.

Conclusion

We have investigated crystals with a complex lattice and a large number of vibrational modes and shallow impurity states, at which excitons were bound, and the structure of the edge absorption was due to many optical transitions. The absorption spectra due to these transitions superimposed each other and resembled interference effects.

References

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